Final Report

Tittabawassee River Floodplain Scoping Study Work Plan

Prepared for

The Dow Chemical Company

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Contents

Appendix

Tables

Figures (located at the end of each section)

Acronyms and Terms

ANOVA	analysis of variance
bgs	below ground surface
CCR	*Tittabawassee River and Floodplain Current Conditions Report*
CSM	conceptual site model
Dow	The Dow Chemical Company
DQOs	data quality objectives
Facility	Dow Michigan Operations-Midland Plant in Midland, Michigan
GPS	global positioning system
H_0	null hypothesis
MDEQ	Michigan Department of Environmental Quality
MS/MSD	matrix spike/matrix spike duplicate
PCBs	polychlorinated biphenyls
PCOI	preliminary constituent of interest
QAPP	Quality Assurance Project Plan
QC	quality control
RI	remedial investigation
SOPs	Standard Operating Procedures
SVOCs	semivolatile organic compounds
TEF	Toxic Equivalency Factor
TEQ	toxic equivalent
TOC	total organic carbon
TSS	total suspended solids
USEPA	U.S. Environmental Protection Agency
VOCs	volatile organic compounds

1.0 Introduction

This Tittabawassee River Scoping Study Work Plan presents the project approach and sampling designs for investigations to support refinement of the conceptual site model for the Tittabawassee River downstream of the The Dow Chemical Company (Dow) Michigan Operations-Midland Plant (Facility) in Midland, Michigan. These scoping investigations are designed to make a preliminary assessment of the relationships between river sediment and adjacent floodplain soil and to determine the geospatial predictability of dioxin and furan distribution in floodplain soil. The information generated from these investigations will be used to support design of the full-scale remedial investigation (RI) for this offsite study area.

1.1 Background

The portion of the Tittabawassee River and floodplain that make up the study area covered in this SAP extends approximately 22 miles southeast from the upstream boundary of the Facility to the confluence of the Tittabawassee and Shiawassee Rivers (Figure 1-1). This area is located within Midland and Saginaw Counties. Several studies have been conducted to characterize aspects of the environmental conditions along the Tittabawassee River. Of the investigations conducted to date, the baseline chemical characterization study of the Saginaw Bay Watershed Area, conducted by Michigan Department of Environmental Quality (MDEQ) in 2001 (MDEQ 2002a), was the most extensive with respect to media and target analytes. The study included analysis of sediment and floodplain soil samples for volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), pesticides, polychlorinated biphenyls (PCBs), dioxins and furans, and metals. Of these target analytes, only dioxins and furans were detected above background levels and/or at consistently high levels (MDEQ 2002a).

1.2 Scoping Study Investigation Purpose and Objectives

The overall goals of the RI will be consistent with the Part 201 purpose "… *to assess site conditions in order to select an appropriate remedial action.*" This will require sufficient characterization of the nature and extent of dioxin and furan contamination to support evaluation of potential risks posed by those contaminants to human and ecological receptors. Because uncertainties and data gaps exist in our understanding of current site conditions and the existing preliminary conceptual model, additional information is needed to appropriately scale and scope the RI.

The key issues, and the studies proposed within this scoping study to address them are:

- What is the relationship between geospatial factors (geomorphology, distance from the river, land use and disturbance) and dioxin and furan concentrations in floodplain soils? This will be addressed by the Floodplain Soils Characterization Study.
- What is the relationship between the dioxins and furans in sediments and the occurrence and distribution of dioxins and furans in floodplain soils? This will be addressed by the Sediment and Floodplain Soil Assessment.

- Are there trends in dioxin and furan concentration and distribution in soils within the confluence area between the Tittabawassee and Shiawassee Rivers? This will be addressed by the Confluence Area Exploratory Assessment.
- How are solids-bound dioxins and furans gained or lost in the lower Tittabawassee River over the course of a typical wet weather event? This will be addressed by the Instream High-Volume Sampling Program.

Data quality objectives (DQOs) linked to these key issues have been developed to provide the rationale for the specific studies proposed in the scoping study investigation. The DQOs are presented in Appendix A. Data gathered during the investigations detailed in this SAP will be supplemented by additional physical and chemical data gathered in the Tittabawassee River and the floodplain by other existing investigations.

1.3 Sampling and Analysis Plan Organization

This SAP is organized as follows:

- Section 1 presents an introduction to the Tittabawassee River study area and identifies the project objectives.
- Section 2 provides the linkage between the data needs for supplementing the conceptual site model and the planned sampling and data evaluation methodologies.
- Section 3 presents the project implementation schedule.
- Section 4 lists references cited in this SAP.

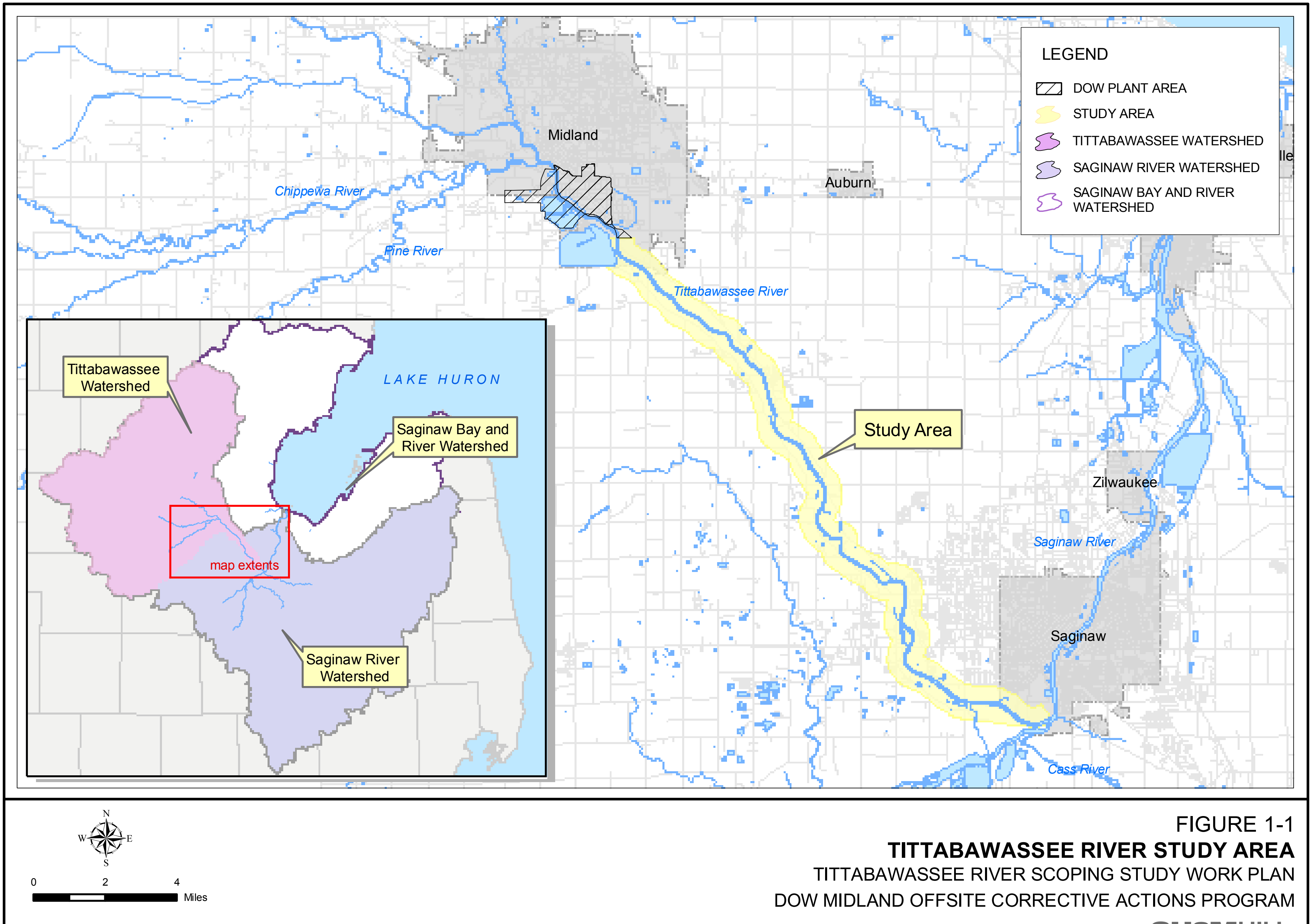

FIGURE 1-1
TITTABAWASSEE RIVER STUDY AREA
TITTABAWASSEE RIVER SCOPING STUDY WORK PLAN
DOW MIDLAND OFFSITE CORRECTIVE ACTIONS PROGRAM

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2.0 Sampling Designs and Data Evaluation Methodology

Certain conditions and processes within the river and along its floodplain must be better understood to design an appropriately scoped remedial investigation for the site. The following data collection and evaluation activities will be conducted as part of the scoping investigation to support refinement of the conceptual site model:

- Characterization of geomorphologic features, distance from the river channel and land use within three floodplain study areas to support development of a geostatistical model for dioxin and furan distribution in Tittabawassee River floodplain soils
- Assessment of sediment and floodplain soil interrelationships
- Exploratory assessment of dioxin and furan trends in surface soil within the confluence area between the Tittabawassee and Shiawassee Rivers
- Instream high-volume sampling to characterize sediment loads entering and leaving the Tittabawassee River

The following sections detail the objectives, sampling designs, and evaluation procedures for each listed activity.

2.1 Floodplain Soils Characterization Scoping Study

Review of historical data suggests that the distribution of dioxins and furans in floodplain soils may be related to geomorphology, land use, and distance from the river channel. If this is true, these relationships could be used to develop a model to predict distribution of dioxins and furans throughout the floodplain. However, the existing data were not collected to meet this objective and are not collected spatially or systematically enough to test the current hypotheses and relationships. The objective of the floodplain soils scoping study is to systematically collect data to support statistical evaluations that will aid in understanding the spatial variability in dioxin and furan distribution in floodplain soil so that an effective RI sampling plan can be developed for the Tittabawassee River floodplain.

As detailed in Appendix A, the following null hypothesis (H_0) will be tested using data collected during the floodplain scoping study:

> H_o: The distribution of contaminants in floodplain soils is not readily predictable.

The alternative to the null hypothesis consists of the following:

> H_1: Geomorphology, land use and distance from the river channel along and within the floodplain influence distribution of contaminants within floodplain soils in a predictable manner.

If the alternative hypothesis reflects site conditions, then the distribution and concentration of dioxin and furan throughout the Tittabawassee floodplain can be evaluated using geostatistical analysis techniques.

2.1.1 Sampling Design

MDEQ recommends a combination of sampling strategies to address complex, dynamic environmental systems such as the Tittabawassee River and floodplain (MDEQ 2002b). Consistent with this guidance, the floodplain scoping study uses a multiphased approach that includes a combination of random sampling and judgmental sampling to develop an initial understanding of the distribution of dioxins and furans along the Tittabawassee River floodplain.

The design of the floodplain scoping study sampling program is based on the anticipated use of geostatistics to predict dioxin and furan distribution and concentrations in floodplain soil. A geostatistical model will be based on geospatial, physical, and chemical data obtained at both regularly spaced and randomly positioned sampling locations. Geostatistics is a branch of statistics that describes spatial relationships in samples collected from different locations, and uses those relationships (statistical models) to predict unknown quantities in unsampled areas. A typical geostatistical evaluation involves the construction of semivariograms, or simple models of the correlation structure of sampling data. The semivariogram is used to determine the typical distances over which data are spatially correlated (range), and the orientations of the major and minor directions of correlation. These correlation ranges can provide an estimate of the typical size of contaminant deposits, and if well-defined semivariograms can be developed, an appropriate spacing for future samples can be determined.

Semivariograms define the correlation range and orientation parameters of the spatial models used to perform spatially correlated interpolation, or kriging. Kriging optimally weights measurements from sampled locations to estimate concentrations at unsampled locations, while preserving the correlation structure described by the semivariogram. "Block" kriging can be used to develop an exposure point concentration for an assumed finite exposure area for risk assessment purposes. Ultimately, an appropriately applied geostatistical evaluation can provide interpolated concentration estimates that are true to individual data points and also reproduce the ranges of spatial correlation observed in the data. Kriging also provides a way to estimate the uncertainty in interpolated data.

Three scoping study areas located along the Tittabawassee River floodplain were identified for study. The three areas shown in Figure 2-1 were chosen so that samples could be collected from increasing distances downstream from the Dow Facility so that the influence of distance on concentration and distribution could be evaluated along with changes in river and floodplain characteristics. The Tittabawassee River changes in characteristics from upstream to downstream. In its upper reaches, the river tends to run in a straight line and the floodplain is relatively narrow. As the river nears its confluence with the Shiawassee and Saginaw Rivers it begins to exhibit a degree of sinuosity and the floodplain widens considerably. The scoping study area locations are representative of these different areas. Additionally, the selected study areas contain features that, based on a preliminary evaluation of available data, appear to influence dioxin and furan distribution in soil, such as distance from the Tittabawassee River, floodplain geomorphologic features (e.g., presence or absence of natural levees), soil characteristics, land use, and disturbance following deposition. The influence of these various factors on dioxin and furan concentration and distribution within the floodplain will be evaluated using samples collected from each scoping study area. The following sample design will be applied to each floodplain scoping study area:

- An initial grid sampling program (Round 1) to systematically collect data that will be used to evaluate the distribution of dioxins and furans in surface soil
- A geostatistical cluster investigation (Round 2) to test various spatial relationships associated with the distribution and concentration of dioxin and furans found in floodplain soils in specific subareas or domains

Scoping Study Area Grid Sampling Design

The scoping area grid sampling design is based on a systematic random sampling approach. A random approach requires little or no prior knowledge of material distribution and relies on random chance probability theory, where each sampling location has an equal and known probability of being selected so that sampling error can be accurately estimated (MDEQ 2002b). Systematic random sampling is an extension of simple random sampling, but is more efficient in that it introduces a systematic element (that is, regular spacing of locations, initiated from a random starting point) to the program, assuring uniform coverage of the entire area being characterized.

The design for each scoping study area consists of a relatively coarse (400-foot spacing) sampling grid deployed across an area that includes relatively equal proportions of "disturbed" (i.e., cultivated) and "undisturbed" (i.e., forested) land located near and distant to the bank of the river. Each grid was laid out to roughly parallel the river and was extended into certain areas to allow collection of roughly equivalent numbers of samples for each potential factor grouping (i.e., near/far, disturbed/undisturbed). Approximately 40 surface soil (0 to 0.5 feet below ground surface [bgs]) samples will be collected in each scoping study area.

The proposed surface soil sample locations for each scoping study area are shown as yellow circles and yellow squares on Figures 2-2, 2-3, and 2-4.

Representativeness of the 400-foot-grid spacing will be evaluated through collection of collocated samples. The collocated samples will be placed to reflect the different hypotheses regarding factors that influence contaminant distribution, including the following:

- Locations near the Tittabawassee River where depositional features are present
- Locations further away from the Tittabawassee River where depositional features are not present
- Locations in disturbed areas (e.g., agricultural land)
- Locations in undisturbed areas (e.g., forested property)

Collocated samples that are representative of these four floodplain conditions will be randomly selected from the overall floodplain sampling grid in each scoping study area. The locations for collocated samples will be randomly generated using the Microsoft Excel "RAND" function to identify the grid node, orientation angle and distance (random distances that are less than or equal to half the distance to the next closest grid node) between the collocated and the original grid node samples.

The grid node and collocated samples will be analyzed for dioxins and furans (17 congeners), total organic carbon (TOC), and grain size.

Cluster Sampling

The initial grid sampling results will be evaluated to identify several locations within each scoping study area for cluster sampling during Round 2. Cluster sampling will be conducted at locations that represent the various spatial relationships being tested (e.g., near river, disturbed) and nodes with elevated and low-to-moderate dioxin/furan concentration will be represented in this sampling program.

The second round of soil sampling will be configured as clusters of surface soil samples arrayed around the original grid nodes established in the first round of sampling. A total of 20 cluster samples will be collected around each selected grid node. Typically, the cluster sample locations will be placed around the central sample at logarithmically increasing distances (1, 10, 30, 100, and 300 feet) and extending radially in four different directions (parallel, and perpendicular to the Tittabawassee River). However, the orientation, spacing, and extent of each cluster array will be adjusted to ensure that cluster sample locations fall within an area that represents the spatial relationship being tested.

The irregular pattern of the cluster samples assures that a range of sampling distances and directions are available to model a two-dimensional semivariogram and to perform analysis of variance (ANOVA). The shape of the directional semivariograms will help to define the optimal sampling distance in the two directions defining the spatial anisotropy. The correlation patterns observed in the range of sampling distances in the clusters and grid will dictate the optimal sampling distance for the entire floodplain study area, to be implemented in a future phase or phases of sampling. Optimal distance is defined as the distance that is close enough for reliable interpolation of concentrations and local trends in any direction. This approach, combining a regular grid with clusters, is similar to the one empoyed by the MDEQ and U.S. Environmental Protection Agency (USEPA) Region 5 used to evaluate the Kalamazoo River former impoundment soils.

The cluster samples will analyzed for dioxins and furans (17 congeners), TOC, and grain size.

2.1.2 Sampling Procedures

The grid and cluster soil samples will be obtained using a hand auger. Decontaminated or disposable equipment will be used to collect soil and transfer it to appropriate sample containers. The activities associated with the sampling activities will be documented in field logbooks. The procedures and quality control (QC) procedures for sampling and field logbook entries are located in the Field Standard Operating Procedures (SOPs) (CH2M HILL 2004a) and Quality Assurance Project Plan (QAPP) (CH2M HILL 2004b).

2.1.3 Physical and Chemical Data to be Gathered at Each Location

The global positioning system (GPS) location, elevation, sample interval, description, and general site features will also be recorded for each sample and core location. Soil and sediment samples collected for chemical analysis will be analyzed for dioxins and furan congeners (17 congeners) using SW-846 8290/EPA Method 1613, grain size, and TOC.

The sample container and preservation requirements are presented in Table 2-1. Additional sample container and preservation requirements are given in the QAPP (CH2M HILL 2004b).

2.1.4 Data Evaluation

Data developed under this effort will be used to develop directional semivariograms describing correlation ranges in directions parallel and perpendicular to the river and floodplain. If the semivariograms indicate significant correlation structure, the identified ranges will help to define optimal sampling distances in the two directions. Observations of these ranges as well as the dependence of contaminant concentrations on the different spatial factors will support preparation of a geostatistically based model that can be used to predict concentrations of dioxin/furans in soil along the floodplain. Correlations between contaminant concentrations and other potentially related factors (e.g., TOC, grain size distribution parameters, flood recurrence) will also be explored, as possible additional constraints to the geostatistical model. If such secondary correlation relationships are identified, these data may provide the basis for development of a more robust co-kriging model that can be constrained with significantly less expensive physical data.

In parallel with the geostatistical analysis of the data, an ANOVA will be used to explore differences in the distribution of dioxins and furans within the different floodplain type classifications (e.g., forested) described above. ANOVA is a standard statistical technique used to determine differences among populations or subgroups of interest. The method relies on differences in variance both across and within subpopulations of interest. "Nested ANOVA" is a technique that explores overlapping sources of variability in the data. In the floodplain soils scoping study sampling, sources of variability include the following:

- Laboratory measurements (as estimated by laboratory duplicate results)
- Sampling techniques, commonly referred to as "sampling error" (as estimated by field duplicate results)
- Small-scale variability in concentrations (as estimated by collocated samples)
- Larger-scale variability in concentrations (as estimated by the samples collected at different grid node locations) within a sampled area
- Larger-scale variability in concentrations among sampled areas (as estimated by samples collected from different portions of the scoping areas [e.g., disturbed versus undisturbed areas and areas close to the bank versus areas distant from the river])

The results of the ANOVA will provide information on statistical differences between contaminant concentrations in subgroups of interest in the floodplain (e.g., statistical difference between concentrations in disturbed versus undisturbed areas). This information, along with other investigations of contaminant fate and transport processes, will be used to refine the current CSM and plan full-scale sampling of the Tittabawassee River floodplain soils as part of the development of the RI Work Plan.

Verification sampling will be conducted at selected locations in each scoping study area to gauge the ability of the developed models to predict contaminant concentrations. The developed semivariogram relationships and geostatistical model will be used to design the sampling plan for the Tittabawassee floodplain study area.

2.2 Assessment of Sediment and Floodplain Soil Relationships

The objective of the floodplain and river transect portions of this scoping study is to assess conditions at the surface and at depth in floodplain soils and river sediments to better understand the relationships between floodplain soils and adjacent river sediment.

As detailed in Appendix A, the following pairs of null and alternate hypotheses will be tested using data collected from the floodplain and river transect study:

1. H_{0A}: Floodplain soil and river sediment do not share similar lithologic and physical characteristics.

   H_{1A}: Floodplain soils and river sediments share similar lithologic and physical characteristics, suggesting a direct relationship between floodplain soils and adjacent river sediments.

2. H_{0B}: Floodplain soils and river sediments do not have similar dioxin and furan distributions at depth.

   H_{1B}: Surface and subsurface floodplain soil and river sediment have similar dioxin and furan distributions, suggesting a direct relationship between floodplain soils and adjacent river sediments.

3. H_{0C}: Rates of sediment deposition on the floodplain in the lower portion of the Tittabawassee River are not similar to those in the upper portion of the river.

   H_{1C}: Rates of sediment deposition on the floodplain in the lower portion of the Tittabawassee River are similar to those in the upper portion of the river, indicating a common pattern of sediment deposition throughout the floodplain.

2.2.1 Sampling Design

A transect that goes through and adjacent to each of the three scoping study areas will be established. Samples will be collected along each transect and the data generated from these samples sets will be used to test the three hypotheses listed above. These samples will be collected as part of the Round 1 investigation. The sampling design for the floodplain soil and river sediment sampling program is as follows:

- **Lithologic Core Transect Sampling.** To test the first set of hypotheses, subsurface lithologic borings will be placed along transects that span each scoping study area. Soil cores will be advanced using direct-push techniques to a depth consistent with 4 feet below the riverbed adjacent to the scoping study area (bottom of river/top of sediment will be determined from bathymetry data), or 2 feet into the underlying glacial till, whichever is encountered first. The soil cores will be obtained at 200-foot intervals along each scoping study area transect (red triangles on Figures 2-2, 2-3, and 2-4). Sediment cores will be collected at three locations spanning the river (blue circles on Figures 2-2, 2-3, and 2-4). The sediment cores will be advanced using vibracoring (or similar technique) to the depth at which unconsolidated material is no longer present and consolidated native material is encountered.

- **Vertical Characterization Sampling.** The second set of hypotheses will be tested by selecting a subset of the soil cores and all sediment cores from the lithologic core transect sampling program and segmenting them into 0.5-foot (upper 3 feet) and 1-foot (remainder of core) intervals. Initially, each 6-inch interval from a core will be analyzed to determine the concentrations of dioxins and furans (17 congeners) and TOC. Grain size analysis will also be performed. The need for analysis of the deeper samples will be determined by the results for the preceding sample interval (e.g., if dioxins and furans are detected in the 3.0 to 4.0-foot interval, then the 4.0- to 5.0-foot sample will be analyzed). The vertical characterization soil cores will be obtained using direct push equipment at transect locations that represent the geospatial (i.e., near the river, far from the river) and land use (i.e., disturbed or undistributed) elements discussed into the geospatially-based design for floodplain characterization described in Section 2.1.1. Preliminary locations for the vertical characterization samples are shown as blue squares on Figures 2-2 through 2-4.

- **Sediment Deposition Evaluation.** Data will be collected from Scoping Study Area 3 to evaluate the rate of deposition on the floodplain. This information will be used to test the third set of hypotheses listed in Section 2.2. These data will supplement dendrogeomorphic and geochronological data collected under a previous effort in Scoping Areas 1 and 2. These deposition evaluation techniques are based on the following considerations:

  – Dendrogeomorphic measurement techniques are based on the general observation that primary lateral roots of selected species of tree are typically located at or near the ground surface at germination of the tree, and remain at approximately the same vertical elevation throughout the life of the tree (see Figure 2-5). This characteristic makes it possible to excavate down to the primary laterals and compare the depth of deposited soils with the age of the tree (obtained by coring the tree and counting rings) to determine a net deposition rate over the tree's lifespan. Studying trees of different ages in the same location allows one to detect changes in deposition rates over time as well. Deposition rates measured with this method are less sensitive to the disturbances that can confound radionuclide-based measurements. Dendrogeomorphic measurements will be taken from three locations along an undisturbed portion of the lithologic core transect in Scoping Study Area 3.

  – Geochronological estimates of deposition rates will be determined by examining vertical profiles of lead-210, which exhibits a profile of exponential decay with depth in consistently deposited sediments, and cesium-137, which can exhibit concentration peaks at depth that correspond to peak atmospheric fallout related to nuclear weapons testing in the early 1950s and 1960s. The cesium and lead data will also be used in evaluating the spatial variability in deposition rates that could be related to hydrodynamics of the river and to correlate depositional dates with vertical characterization data. The process for identifying and isolating individual core segment intervals for geochronological analysis is illustrated in Figure 2-6. Five samples be will collected for geochronological analyses in Scoping Study Area 3. These samples will be collected near the trees selected for the dendrogeomorphic study.

2.2.2 Sample Procedures

The subsurface soil cores and samples will be obtained using direct-push technology. Decontaminated or disposable equipment will be used to collect soil and transfer it to appropriate sample containers. The activities associated with the sampling activities will be documented in field logbooks. The procedures and QC procedures for sampling and field logbook entries are located in the Field SOPs (CH2M HILL 2004a) and QAPP (CH2M HILL 2004b).

2.2.3 Physical and Chemical Data to be Gathered at Each Location

The GPS location, elevation, sample interval, description, and general site features will also be recorded for each sample and core location. Soil and sediment samples collected for chemical analysis will be analyzed for dioxins and furan congeners (17 congeners) using SW-846 8290/EPA Method 1613, grain size, and TOC. Soil samples collected for geochronological analysis will be analyzed for cesium-137 and lead-210.

The sample container and preservation requirements are presented in Table 2-1. Additional sample container and preservation requirements are given in the QAPP (CH2M HILL 2004b).

2.2.4 Data Evaluation

Data gathered under the lithologic coring investigation, the vertical characterization investigations, the geochronological and dendrogeomorphic evaluations will be used to assemble an improved understanding of river and floodplain geomorphology along the each detailed transect, and the recent and historical depositional characteristics of the transects. Development of these data will help to establish the influence of sediment transport on the distribution of dioxin and furan in the river floodplain.

2.3 Confluence Area Exploratory Assessment

Hydrological conditions in the confluence area between the Tittabawassee and Shiawassee Rivers are poorly understood and it is uncertain whether geostatistical models developed for the upper reaches of the river would be applicable to this portion of the study area.

The objective of the confluence area sampling program is to obtain data that will be used to better understand sedimentation rates and trends in dioxins and furan distribution in surface soil in the lower portions of the Tittabawassee River study area. As detailed in Appendix A, the following pairs of null and alternate hypotheses will be tested using data collected during the confluence area exploratory assessment:

1. H_{0A}: Rates of sediment deposition on the floodplain in the lower portion of the Tittabawassee River are not similar to those in the upper portion of the river.

   H_{1A}: Rates of sediment deposition on the floodplain in the lower portion of the Tittabawassee River are similar to those in the upper portion of the river, indicating a common pattern of sediment deposition throughout the floodplain.

2. H_{0B}: Trends in dioxin and furan concentrations across the confluence area are not related to distance from the Tittabawassee River.

   H_{1B}: Trends in dioxin and furan concentrations across the confluence area are related to distances from the Tittabawassee River, and this information can be used to help develop the remedial investigation of the Tittabawassee River.

3. H_{0C}: Trends in dioxin and furan concentrations across the confluence area are not related to frequency of flooding.

   H_{1C}: Trends in dioxin and furan concentrations across the confluence area are related to frequency of flooding, and this information can be used to help develop the remedial investigation of the Tittabawassee River.

2.3.1 Sampling Design

The exploratory assessment will consist of a sediment deposition evaluation and a surface soil sampling program. The surface soil sampling program will be conducted along two mutually perpendicular transects through the Confluence Area (Figure 2-7):

- Exploratory Transect A consists of a north-south trending line extending from Scoping Study Area 3 through the Confluence Area to the southern bank of the Shiawassee River. Data from surface soil (0 to 0.5 feet bgs) along Transect A will be used to identify trends in dioxin and furan distribution that may be related to distance from the Tittabawassee River and/or proximity to the Shiawassee River. The soil sampling design for Transect A consists of collecting surface soil samples at a spacing of 400 feet near the Tittabawassee River (replicating the grid spacing in Scoping Study Area 3) and at a spacing of 800 feet further away from the Tittabawassee River.

- Exploratory Transect B consists of west-east trending line crossing a portion of the floodplain where the individual floodplains are distinct (e.g., the edge of 10-year floodplain is clearly distinguishable from that of the 100-year floodplain). Data from surface soil (0 to 0.5 feet bgs) along Transect B will be used to identify trends in dioxin and furan distribution that may be related to more frequent recurrence of flooding. Regularly-spaced sample locations along this transect were chosen to represent the gradient from the 1-year floodplain to the 100-year floodplain.

The surface soil samples from the exploratory transects will be analyzed for dioxins and furans (17 congeners), TOC, and grain size.

The sediment deposition evaluation for the confluence area will be similar to that described for Scoping Area 3, in that a dendrogeochronological study will be conducted at three locations along both Transects A and B, and geochronological analysis will be conducted on five 4-feet deep cores taken in the vicinity of the dendrogeochronological study locations along Transects A and B.

The exploratory assessment will be performed during Round 1 of the floodplain soils characterization scoping study.

2.3.2 Sample Procedures

Surface soil samples will be obtained using a hand auger. Subsurface soil cores and samples will be obtained using direct-push technology. Decontaminated or disposable equipment will be used to collect soil and transfer it to appropriate sample containers. The activities associated with the sampling activities will be documented in field logbooks. The procedures and QC procedures for sampling and field logbook entries are located in the Field SOPs (CH2M HILL 2004a) and QAPP (CH2M HILL 2004b).

2.3.3 Physical and Chemical Data to be Gathered at Each Location

The GPS location, elevation, sample interval, description, and general site features will also be recorded for each sample and core location. Soil and sediment samples collected for chemical analysis will be analyzed for dioxins and furan congeners (17 congeners) using SW-846 8290/EPA Method 1613, grain size, and TOC. Soil samples collected for geochronological analysis will be analyzed for cesium-137 and lead-210.

The sample container and preservation requirements are presented in Table 2-1. Additional sample container and preservation requirements are given in the QAPP (CH2M HILL 2004b).

2.3.4 Data Evaluation

Existing data for the Tittabawassee River floodplain suggest that concentrations of dioxins and furans in surficial floodplain soils decrease with distance from the river. Data developed under this effort will be used to identify trends in dioxin and furan concentrations related to flood recurrence and distance from the Tittabawassee and Shiawassee Rivers. If the trends indicate significant correlation structure between one or more of these factors, the structure will be used to define the location and spacing for a scoping study that will be used to test two-dimensional correlation structures in the Confluence Area and elsewhere in the study area where the flood recurrence zones appear separate.

2.4 Instream High-Volume Sampling

Little is currently known about the extent to which dioxins and furans bound to solid particles enter the Tittabawassee River upstream of Midland and are transported downstream to the confluence with the Saginaw River. Also, little is known about the extent to which processes such as floodplain runoff, bank erosion, or exchange with the Tittabawassee River sediment bed contribute to a gain in contaminant load with transport down the river. Hypothesis statements have not been developed for the high-volume sampling effort. The objective of the instream high-volume sampling program is to better quantify the particulate concentration of dioxins and furans at the upstream and downstream boundaries of the study area, as a first step towards quantifying contaminant load gain through the river and floodplain.

2.4.1 Sampling Design

The high-volume water column sampling program will be conducted using samples collected at the Currie Parkway Bridge upstream of the city of Midland, and at the Center Road Bridge just upstream of the confluence of the Tittabawassee River with the Saginaw River. The high-volume water column samples will be collected during high flow events (i.e., flows consistent with a 1 year FEMA flood event of approximately 10,000 cfs or greater) to allow analysis of dioxin and furan concentrations in in-river suspended sediment.

2.4.2 Sample Procedures

Collection of samples will be targeted for the rising limb of the wet weather event, the peak of the event and post-event during the decline of the river hydrograph. Surface water samples will be collected using a depth-integrating isokinetic water sampler (US DH-76). Collected samples will be composited in a 20-liter glass carboy and submitted to a dioxin laboratory for filtration and analysis of dioxins and furan congeners (17 congeners) and for total suspended solids (TSS).

2.4.3 Physical and Chemical Data to be Gathered

The GPS location, elevation, and general site features will be recorded for each sample location. The water samples will be analyzed for TSS and the filtered-out sediment will be analyzed for dioxins and furan congeners (17 congeners). The sample container and preservation requirements are presented in Table 2-1. Additional sample container and preservation requirements are given in the QAPP (CH2M HILL 2004b).

2.4.4 Data Evaluation

Data collected under the instream high-volume sampling effort will be used to quantify the particulate concentrations of dioxins and furans at the upstream and downstream boundaries of the study area, under the range of flow conditions observed during the initial rise, peak, and tail of the monitored wet weather events. Contaminant data will be combined with flow estimates and solids data collected throughout the wet weather event to provide estimated time series of contaminant loads at the upstream and downstream ends of the Tittabawassee River study area. These developed time series will be used to explore how solids-bound contaminants are gained or lost in the lower Tittabawassee River reach over the course of a typical wet weather event, and how these gain or loss processes may change over the course of an event. The analyses will provide a basic understanding of the in-river load gain processes that will be used to support design of a more comprehensive future contaminant mass balance. The proposed sampling program provides basic measurements of upstream contaminant load and in-river load gain that can be used to support design of a more comprehensive future contaminant mass balance

2.5 General Sampling Quality Control and Management Procedures

The following procedures are applicable to each of the sampling programs described in Sections 2.1 through 2.4.

2.5.1 Field Quality Control Samples

Field QC samples will be collected as part of this investigation in accordance with Section 2.5 of the QAPP (CH2M HILL 2004b). QC samples include the following:

- Field blanks, equipment blanks, and matrix spike/matrix spike duplicates (MS/MSDs) will be collected at a minimum frequency of 1 per 20 samples.
- Field duplicates will be collected at a minimum frequency of 1 per 10 samples.

2.5.2 Station/Sample Identification

The general GPS coordinates for locations and sample identification numbers for soil and sediment samples, inclusive of normal and location-based QA/QC sample locations, will be generated upon Dow's approval of this sampling plan. Each station and individual sample will be assigned a unique identifier according to the *Sample Identification Technical Memorandum* (CH2M HILL 2004c). Location and sample identification will be based on specific geographic area codes and record numbers assigned to samples from the Dow Midland data management program.

2.5.3 Sample Handling and Chain of Custody

The procedures used for proper packaging, shipping, and documentation of samples being transported from the field to the laboratory for analysis are provided in the “Sample Handling and Shipping Custody Procedures” of the Field SOP (CH2M HILL 2004a). After samples are labeled and packaged, they will be shipped to the appropriate labs for analysis.

Completed chain-of-custody forms will be required for all samples. The chain-of-custody form will contain the sample’s identification number, sample date and time, sample description, sample type, sample preservation, and analyses required. The original chain-of-custody form will accompany the samples to the laboratory. The forms will remain with the samples at all times. The samples and signed chain-of-custody forms will remain in the possession of the sampling crew until the samples are delivered to the express carrier.

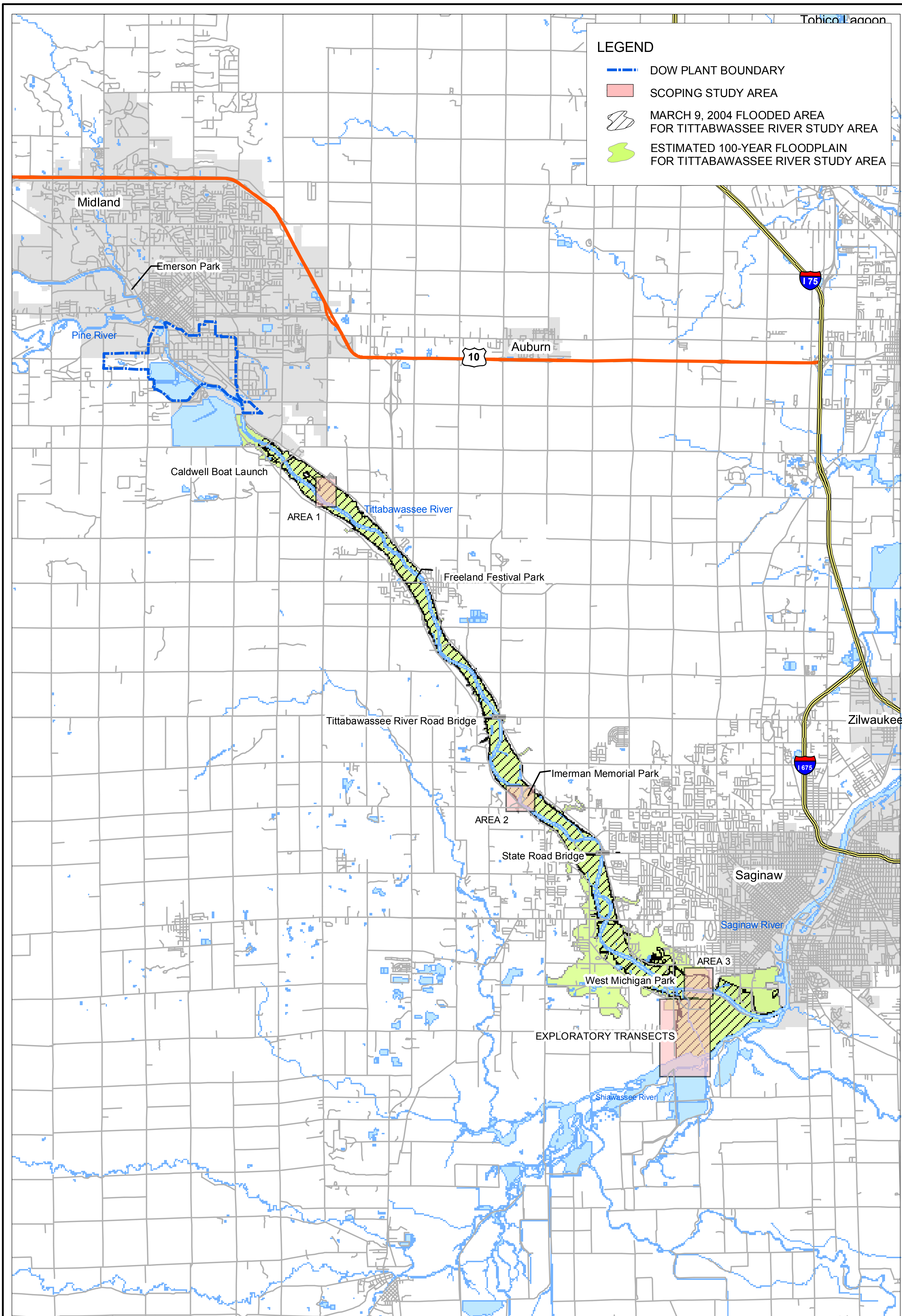
2.5.4 Equipment Decontamination

Personal decontamination procedures will be those given in the *Dow MOCA Health, Safety, and Environment Plan* (CH2M HILL 2003). All soil sampling equipment will be decontaminated in accordance with the “Field Decontamination Procedures” of the Field SOP (CH2M HILL 2004a). Excess soil, disposable sampling equipment, and decontamination materials and liquids will be disposed of in accordance to the “Handling and Disposal of Investigative-derived Waste” Field SOP (CH2M HILL 2004a).

TABLE 2-1
Required Analytical Method, Sample Containers, Preservation, and Holding Times
Tittabawassee River Scoping Investigation SAP
Dow Midland Offsite Corrective Action Program

Analyses	Preparatory/ Analytical Method	Sample Matrix[a]	Container[b]	Qty	Preservative[c]	Holding Time[d]
Total Organic Carbon (TOC)	EPA 415.1/SW-846 9060	W	250-mL polyethylene	1	H_2SO_4 or HCl pH < 2, Cool 4°C	28 days
		S	4-oz glass	1	Cool 4°C	28 days
Dioxins/Furans	SW-846 8290/ EPA 1613	W	1-L amber glass	2	Cool 4°C	30/45 days[e]
		S	8-oz glass	1	Cool 4°C	
Grain Size	ASTM D422	S	8-oz glass	1	None	NA
Dioxins/Furans in Suspended Sediment	SW-846 8290/ EPA 1613	W	20-L glass carboy	1	Cool 4°C	30/45 days[e]
Cs-137	NMN	S	250 mL polyethylene	1	None	NA
Pb-210	NMN	S	250 mL polyethylene	1	None	NA
Dry Bulk Density	Po-01-RC (modified)	S	Same container as above	1	None	NA

Notes:
Sample containers and volume requirements will be specified by the analytical laboratory performing the tests.
Three times the required volume should be collected for samples designated as MS/MSD samples.
[a]Sample matrix: S = surface soil, subsurface soil, sediment; W = surface water
[b]All containers will be sealed with Teflon®-lined screw caps.
[c]All samples will be stored promptly at 4°C in an insulated chest.
[d]Holding times are from the time of sample collection.
[e]30 days to extraction for water, 45 days for analysis.
Source: SW-846, third edition, Update III (June 1997).
°C = Degrees Centigrade
HCl = Hydrochloric acid
HNO_3 = Nitric acid
mL = Milliliter
L = Liter
EPA = U.S. Environmental Protection Agency
NMN = No Method Number
NaOH = Sodium hydroxide
H_2SO_4 = Sulfuric acid
g = Gram
oz = Ounce
ASTM = American Society for Testing and Materials
NA = Not applicable



N
W E
S
0 6,800 13,600
Feet

FIGURE 2-1
OVERVIEW MAP OF SCOPING STUDY AREAS
TITTABAWASSEE RIVER SCOPING STUDY WORK PLAN
DOW MIDLAND OFFSITE CORRECTIVE ACTION PROGRAM
CH2MHILL

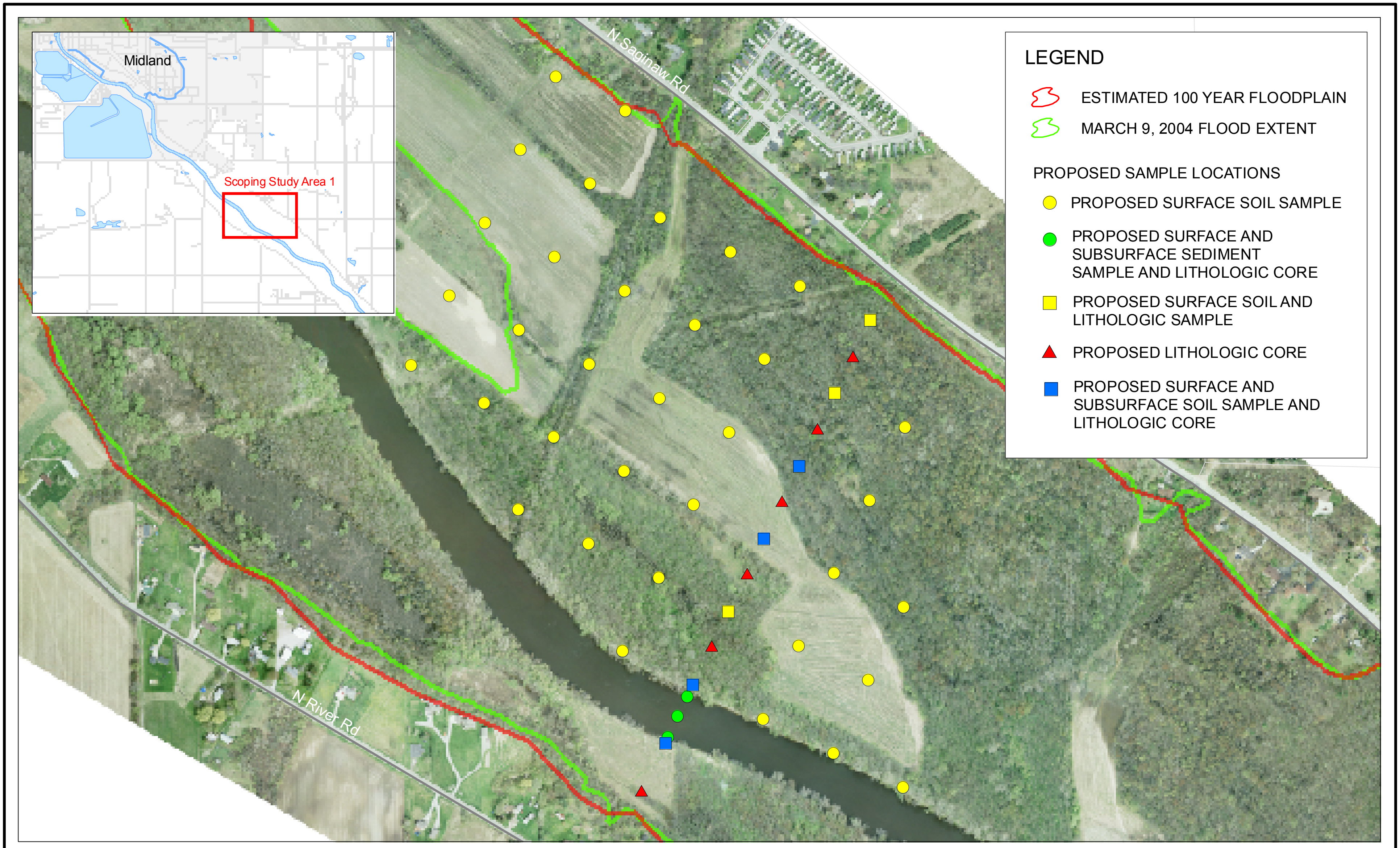


FIGURE 2-2

SCOPING STUDY AREA 1 SAMPLE AND LITHOLOGIC CORE LOCATIONS

TITTABAWASSEE RIVER SCOPING STUDY WORK PLAN

DOW MIDLAND OFFSITE CORRECTIVE ACTION PROGRAM

CH2MHILL

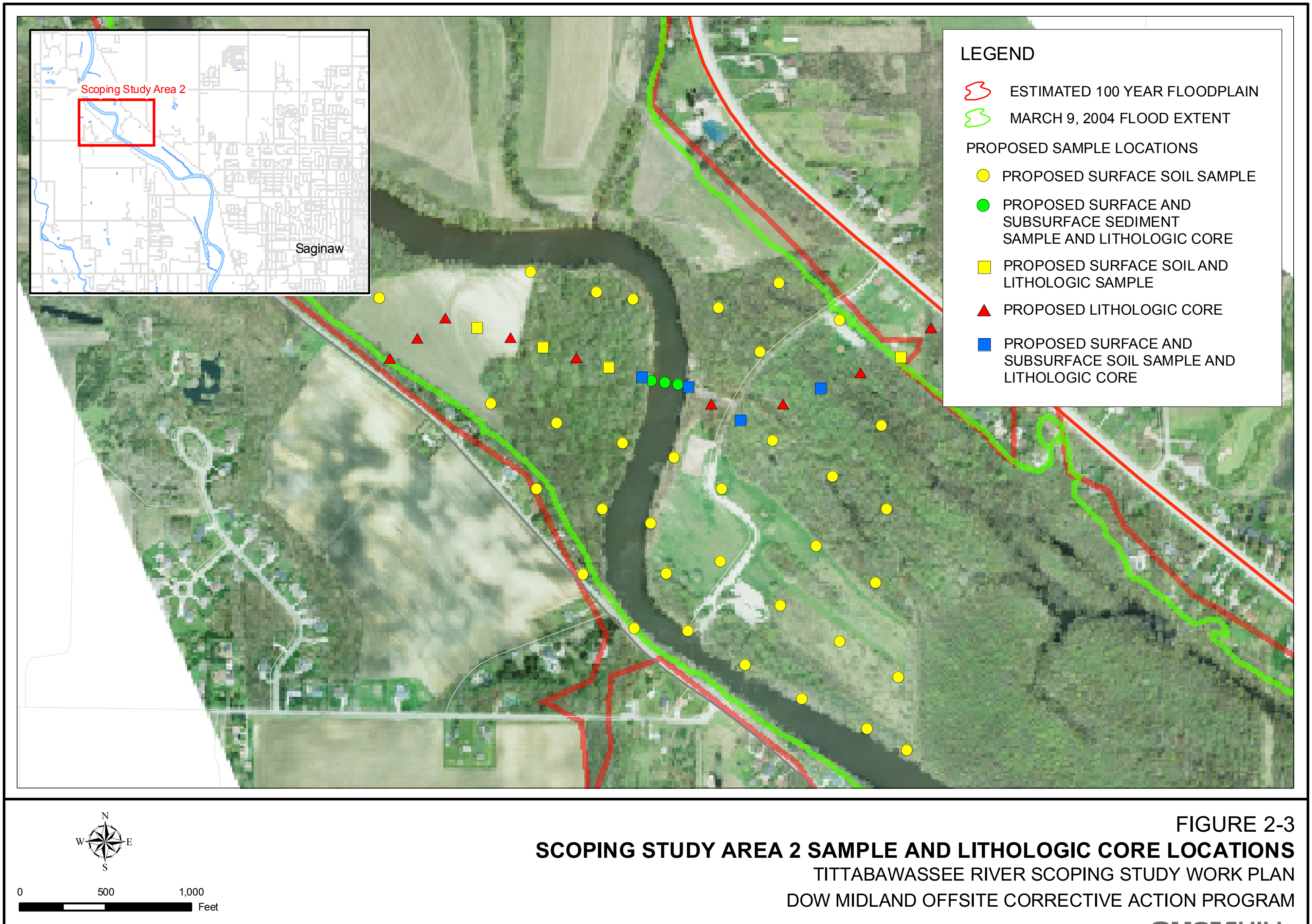


FIGURE 2-3

SCOPING STUDY AREA 2 SAMPLE AND LITHOLOGIC CORE LOCATIONS

TITTABAWASSEE RIVER SCOPING STUDY WORK PLAN

DOW MIDLAND OFFSITE CORRECTIVE ACTION PROGRAM

CH2MHILL

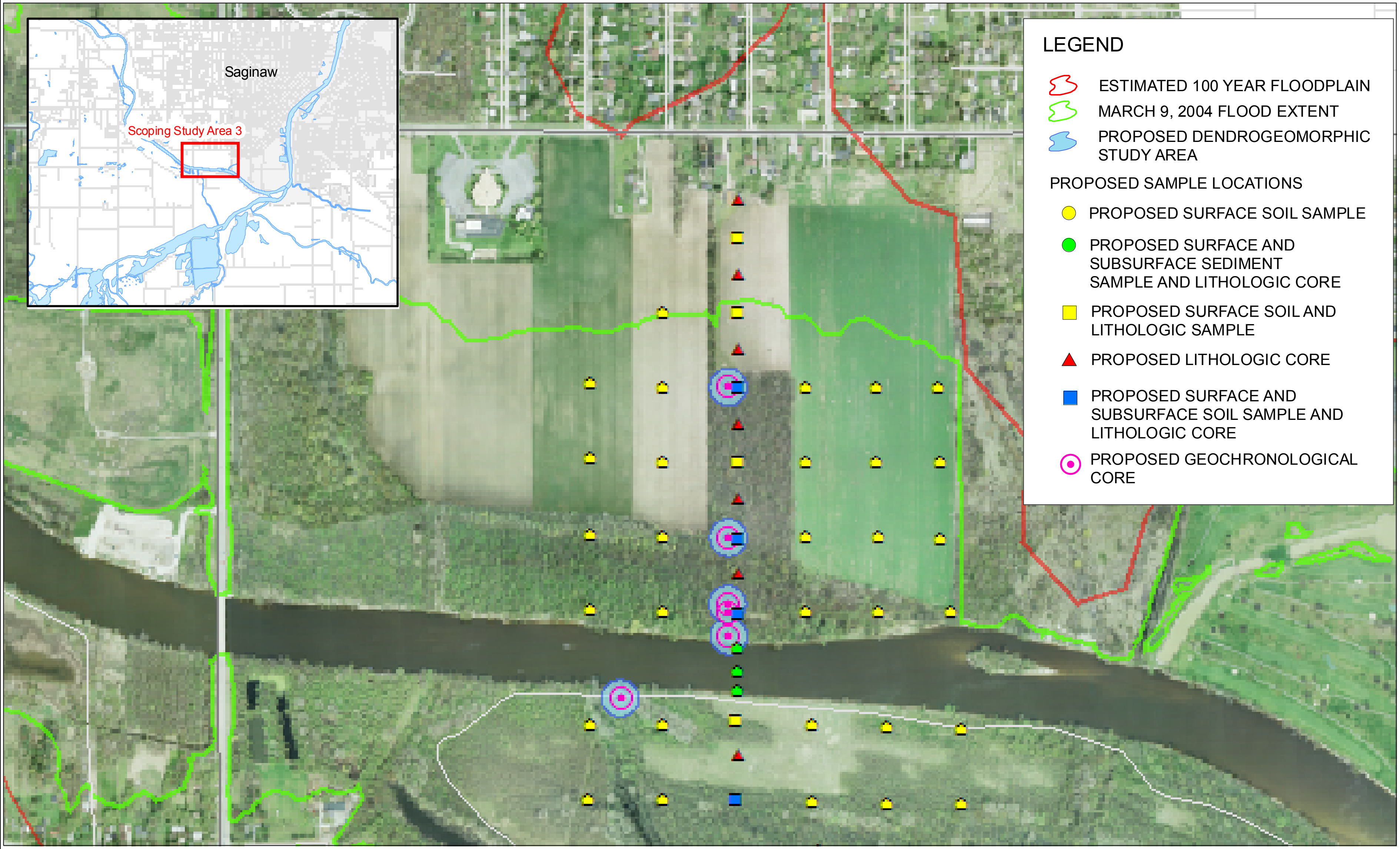


FIGURE 2-4

SCOPING STUDY AREA 3 SAMPLE AND LITHOLOGIC CORE LOCATIONS

TITTABAWASSEE RIVER SCOPING STUDY WORK PLAN

DOW MIDLAND OFFSITE CORRECTIVE ACTION PROGRAM

CH2MHILL

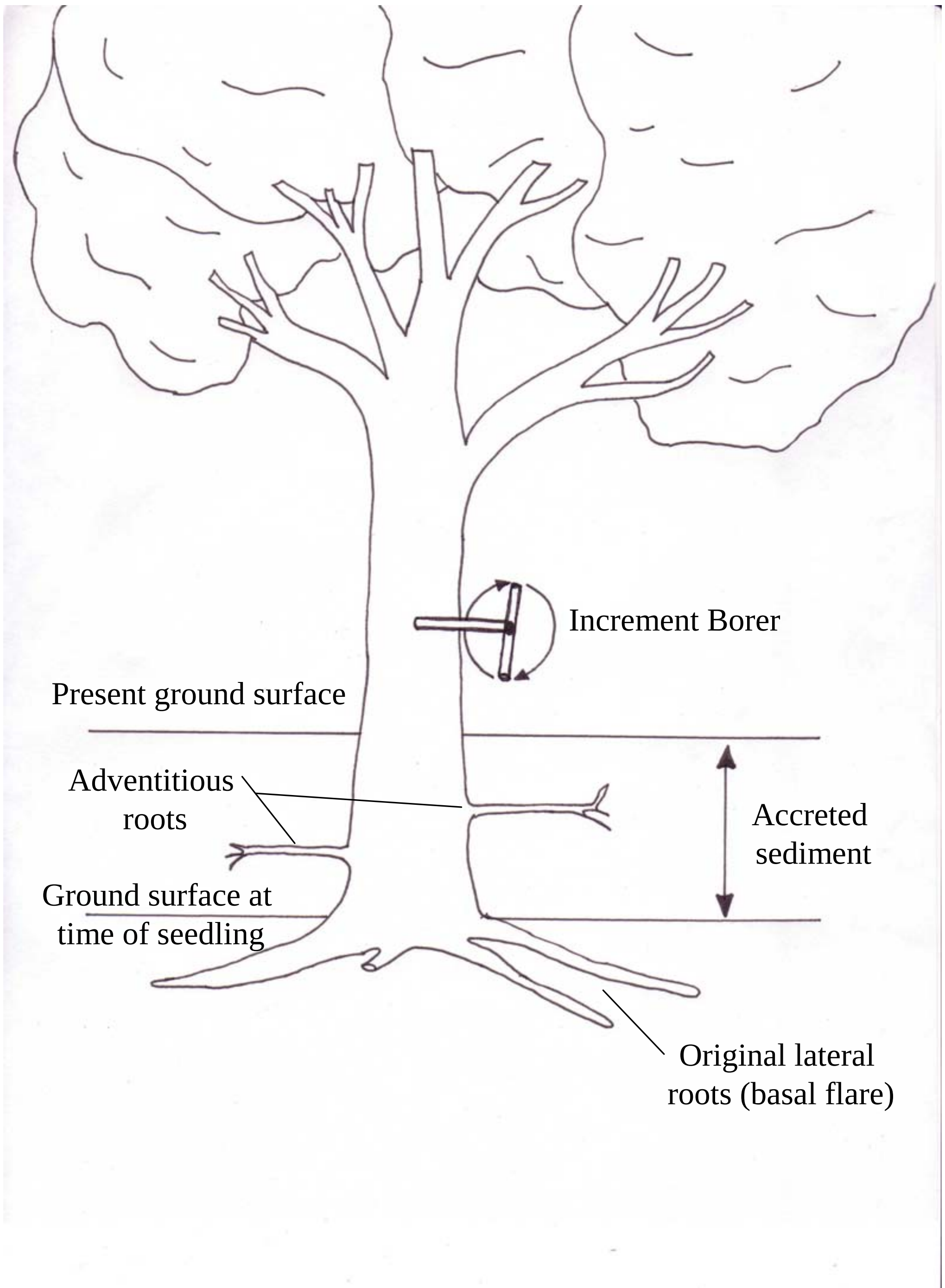


Figure 2-5 Diagram of Dendrogeomorphic Measurement

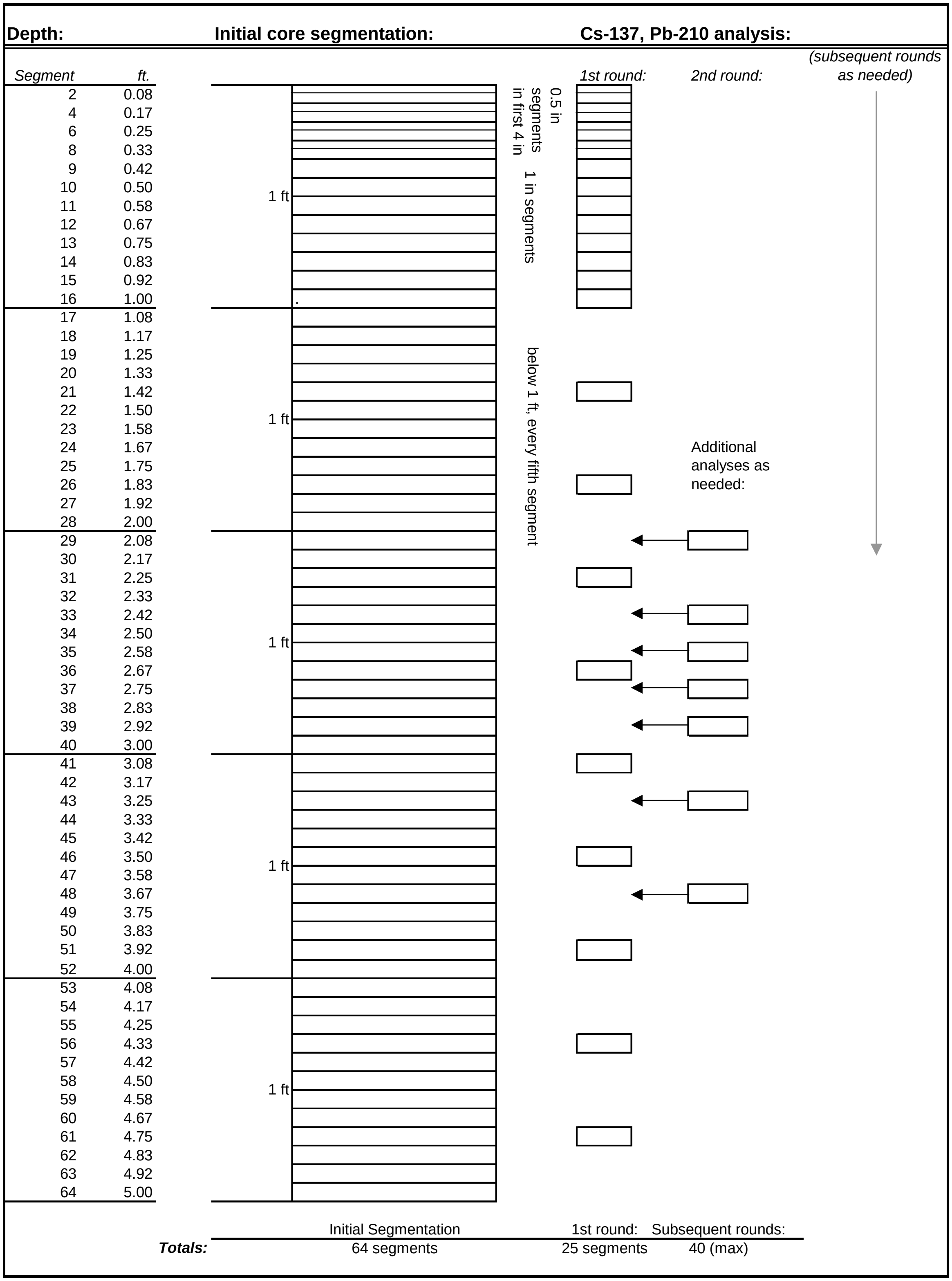
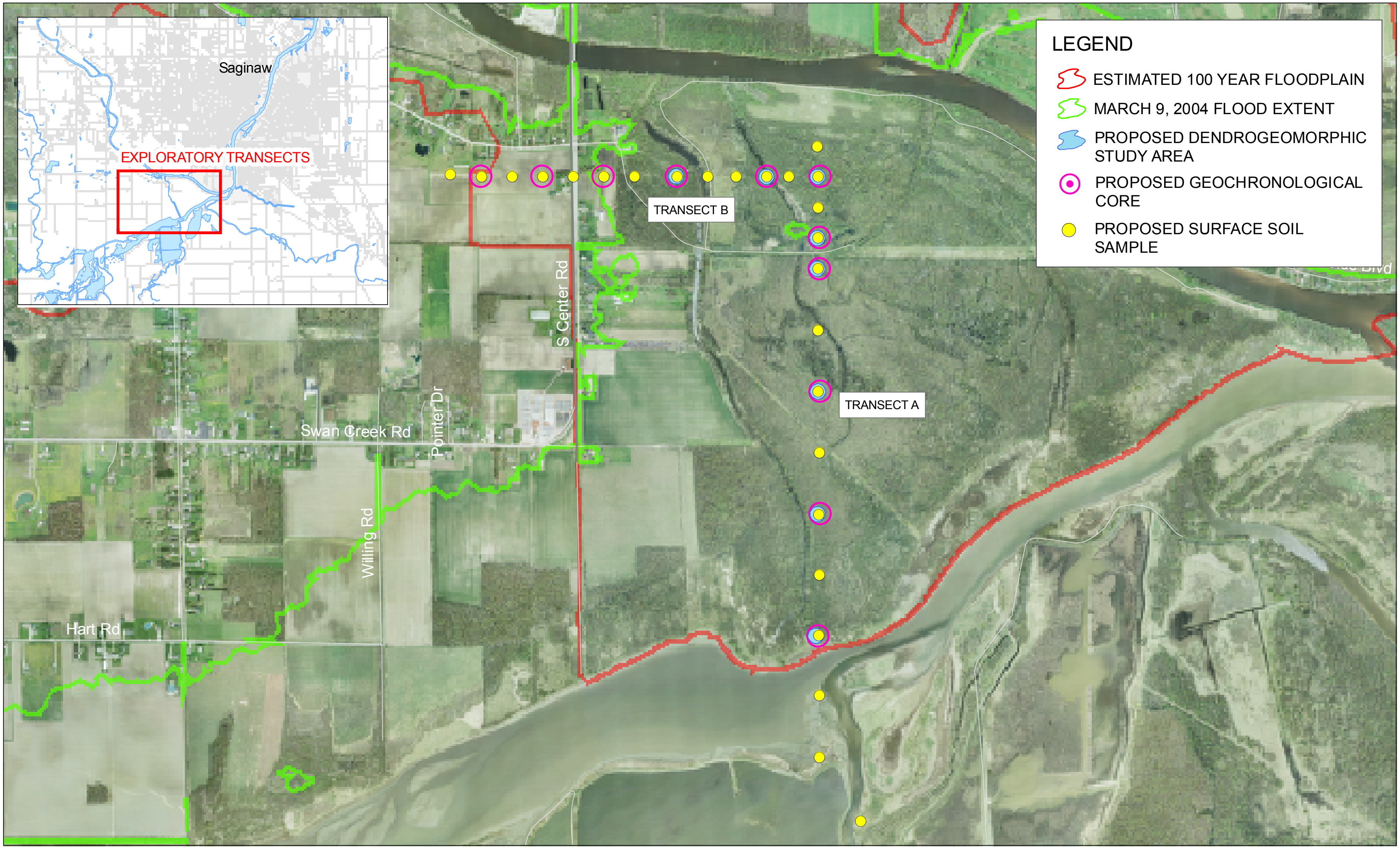


Figure 2-6 Core Segmentation and Analytical Procedure



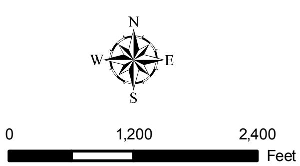


FIGURE 2-7

EXPLORATORY TRANSECTS IN CONFLUENCE AREA

TITTABAWASSEE RIVER SCOPING STUDY WORK PLAN

DOW MIDLAND OFFSITE CORRECTIVE ACTION PROGRAM

CH2MHILL

3.0 Project Schedule

Table 3-1 provides a proposed implementation schedule for activities proposed in this SAP. All investigation activities are planned to be conducted in spring and summer 2005.

TABLE 3-1
Proposed Implementation Schedule
Tittabawassee River Scoping Investigation SAP
Dow Midland Offsite Corrective Action Program

Date	Sample Analysis	Media	Sampling Approach
Round 1 Prepare for Sampling 4/05	Hydrographs, dioxin/furans (grain size (1) and TOC (2) if volume recovered allows)	Surface Water	High Flow Instream Sampling
Round 1 6/13-6/21/05	Dioxin/furans, grain size, TOC	Soils	Scoping Area Grid Sampling
Round 1 6/22-7/6/05	Lithology description	Soils and Sediment	Lithologic Core Transect Sampling
Round 1 6/22-7/6/05	Dioxin/furans, grain size, TOC	Soils and Sediment	Vertical Characterization (along the Lithologic transects)
Round 1 6/22-7/6/05	Soil thickness to lateral tree root and tree core age dating	Soils	Dendrogeomorphology Study
Round 1 6/22-7/6/05	Cs-137, Pb-210, dry bulk density, grain size, TOC	Soils	Geochronological Analysis
7/28-8/3/05	*Scoping Area Grid Sampling results*	*Soils*	*Data evaluation to determine Round 2 cluster locations*
Round 2 8/8– 8/19/05	Dioxin/furans, grain size, TOC	Soils	Cluster Sampling
10/10– 10/21/05	*Incorporate Cluster Area Sampling results into RIWP*	*Soils*	*Geostatistical Model Development*

Italics indicate data evaluation activities

4.0 References

CH2M HILL. 2003. Dow *MOCA Health, Safety, and Environment Plan*. December.

_____. 2004a. *Field Standard Operating Procedures.* April.

_____. 2004b. *Quality Assurance Project Plan.* April.

_____. 2004c. *Sample Identification Technical Memorandum.* March.

Limno-Tech, Inc. 2003. *Work Plan for Preliminary Flow/Solids Monitoring and Sediment Thickness Characterization*. November.

Michigan Department of Environmental Quality (MDEQ). 2002a. *Baseline Chemical Characterization of Saginaw Bay Watershed Sediments*. Michigan Department of Environmental Quality. August 29.

_____. 2002b. *Sampling Strategies and Statistics Training Materials for Part 201 Cleanup Criteria, Remediation and Redevelopment Division*. August.

Rossman, R., C.P. Rice, and M.S. Simmons. 1983. *The Impact of Pollutants on the Tittabawassee River. EPA E-005691-01, 02*. January.

Appendix A
Data Quality Objectives (DQOs) for the Tittabawassee River Floodplain Scoping Study Work Plan

Data Quality Objectives (DQOs) for the Tittabawassee River Floodplain Scoping Study Work Plan

Introduction

The Data Quality Objectives (DQO) process is a planning tool used to ensure that data of sufficient quantity and quality are collected so that informed decisions can be made, and to help avoid collecting data that are inconsequential to decisionmaking. In this manner, DQOs minimize expenditures related to data collection by eliminating unnecessary, duplicative, or overly precise data. DQOs ascertain the type, quality, and quantity of data necessary to address the problem before sampling and analysis begin. The U.S. Environmental Protection Agency (USEPA) guidance document, Guidance for the Data Quality Objectives Process (USEPA 2000) outlines a seven-step process for establishing DQOs. These steps are as follows:

- State the problem. Concisely describe the problem to be solved: background information and what information is missing.
- Identify the decision. Identify the decision that must be made to resolve the problem.
- Identify the inputs to the decision. Identify the information or data needed to make the decision.
- Define the study boundaries. Specify the conditions (time periods, spatial areas, and situations) to which the decision will apply and within which the data will be collected.
- Develop a decision rule. Define the conditions by which the decisionmaker will choose among alternative risk management actions. This is usually specified in the form of an "if. . . then . . ." statement.
- Specify acceptable limits on decision errors. Define the decisionmaker's acceptable uncertainty based on the consequence of making an incorrect decision.
- Optimize the sampling design. Evaluate the results of the previous steps and develop the most resource-efficient design for data collection that meets all of the DQOs.

The data collected during the Tittabawassee River Scoping Study will help to scope and frame the overall Remedial Investigation (RI) for the river and floodplain. A brief description of the RI objectives is presented in this appendix to better define the role of this scoping study investigation in achieving Dow's overall corrective action requirements, as well as describe the linkages between the RI and this scoping study investigation. To ensure that the data collected are suitable for use in developing the RI approach and will support a decisionmaking process, the seven-step DQO process established by USEPA was used to develop the data collection program for this scoping study investigation.

Overview

Investigation Requirements in the Hazardous Waste Operating License

The Hazardous Waste Operating License issued for the Midland Facility by the Michigan Department of Environmental Quality (MDEQ) states that Dow shall implement the corrective action beyond the facility boundary if releases have or may have migrated beyond the facility boundary (Section XI.B.1). The conditions in the license address the characterization of extent of contamination, and assessment of potential human health and ecological risks. The license specifies that a RI will be performed for the Tittabawassee River and Floodplain (IX.F). That RI needs to address the following conditions in the license:

Nature and Extent

XI.B.3(b): ". . . the proposed phasing and prioritization of work . . . based on consideration of the potential risks to human health and the environment" **and** XI.B.3(b)(ii): ". . . identify the specific areas proposed for investigation and the process proposed for selecting these areas." The decisions to be made that address this condition are: (1) determine the initial locations for investigation activities; (2) define the process for identifying additional areas to be investigated, based on results from the initial locations; (3) define the criteria that will be used to indicate when the investigation is complete. XI.B.3(b)(iii): ". . . determine if there are continuing sources of contaminants. . . to the areas identified in Condition XI.B.2. . . [to] include erosional and depositional areas." The decisions to be made that address this condition are: (1) identify locations in the river where elevated concentrations in sediment are most likely to be found; (2) identify locations in the floodplain where flood events are most likely to deposit sediments with elevated contaminant concentrations; (3) evaluate conditions in the river that may contribute to downstream transport of contaminated sediment; (4) evaluate the potential for erosion and transport of floodplain soils to contribute to concentrations in sediments; (5) evaluate the spatial distribution of contaminant concentrations both in floodplain soils and river sediments.

Human Health Risks

XI.B.3(b)(i): ". . .identify additional exposure pathways that do not have Part 201 of Act 451 generic criteria (e.g., food chain exposures, house dust, etc.)" **and** XI.B.3(b)(iv): ". . . propose steps to develop site-specific cleanup criteria, including proposed use of probabilistic risk assessment methods. . . provided they are not less stringent than allowed pursuant to the provisions of RCRA." The decision to be made that addresses this condition is to identify media and locations with chemical concentrations higher than risk-based screening levels, developed using site-specific exposure scenarios. These areas will be evaluated further in a human health risk assessment conducted as part of the RI. The results of the risk assessment will identify those chemicals, media, exposure pathways and receptors that will be addressed in a Feasibility Study, as necessary, using site-specific cleanup criteria.

Ecological Risks

XI.B.3(b)(v): ". . . include provisions for conducting an ecological risk assessment for the areas identified in Condition XI.B.2. . . ". Decisions to be made that addresses this condition include: (1) evaluate physical habitat within the river and define characteristics that affect the presence of ecological receptors; (2) identify the presence of terrestrial receptors in the river and floodplain areas; (3) identify media and locations with chemical concentrations higher than risk-based screening levels, which are based on site-specific exposure scenarios. These areas will be evaluated further in the ecological risk assessment conducted as part of the RI.

Overall Objectives for the Remedial Investigation

The overall objectives of the RI are to characterize the extent of contamination in soil and sediment along the Tittabawassee River and floodplain. The extent of contamination must be understood before evaluating human health and ecological risks, or evaluating possible corrective measures for sediments and floodplain soils. There are data gaps that exist with respect to the extent of contamination in sediments and floodplain soils. These data gaps create difficulties in developing a RI approach for the Tittabawassee River and floodplain.

A phased approach is proposed to address the data gaps; the first phase consists of a scoping study investigation that is designed to answer basic questions regarding the physical site features and fate and transport processes that influence distribution of contaminants in sediments and soils.

Overall Objectives for the Scoping Study Investigation

The key issues, and the studies proposed within this plan to address them are:

- What is the relationship between geospatial factors (geomorphology, distance from the river, land use and disturbance) and dioxin and furan concentrations in floodplain soils?
- What is the relationship between the dioxins and furans in sediments and the occurrence and distribution of dioxins and furans in floodplain soils?
- Are there trends in dioxin and furan concentration and distribution in soils within the confluence area between the Tittabawassee and Shiawassee Rivers?
- How are solids-bound dioxins and furans gained or lost in the lower Tittabawasseee River over the course of a typical wet weather event?

The objective of the scoping study investigation is to develop information that will provide a better understanding of these issues and provide the basis for developing the remedial investigation for the Tittabawassee River and floodplain.

DQOs linked to these key issues have been developed to provide the rationale for the specific studies proposed in the scoping study investigation. The results from these DQOs are data collection designs, which are described in Sections 2.1 through 2.4 of the scoping study.

DQO 1: Understanding Factors Affecting Lateral Distribution of Contaminants in Floodplain Soils

Problem Statement

Preliminary evaluations of available data suggest that the distribution of dioxins and furans in floodplain soils may be related to geomorphology, land use, and distance from the river channel. If this is true, these relationships could be used to develop a model to predict distribution throughout the floodplain. Existing data have not been collected in a systematic enough manner to test this possible relationship. Data will be collected during the scoping study investigation to address the single question (described in the following subsection) associated with this DQO.

Decisions to be Made

The decision to be made (formulated as a testable null hypothesis statement[1]) that addresses the problem statement is:

> H_o: The distribution of contaminants in floodplain soils is not readily predictable.
>
> H_1: Geomorphology, land use and distance from the river channel along and within the floodplain influence distribution of contaminants within floodplain soils in a predictable manner.

If the alternative hypothesis reflects site conditions, then contaminant distribution in soil could be evaluated using geostatistical analysis techniques, and concentrations can be modeled as a function of other observable factors (e.g., geomorphology, land use, distance).

Inputs to the Decisions

To test this problem statement, the following data will be collected in phases:

- Round 1 – collect data in a systematic manner (grid sampling). These data will be used to develop a clustered sampling design for testing the spatial relationships of contaminant concentrations and other physical factors.
- Round 2 – the output from Round 1 becomes the basis for identifying clustered sampling locations. Round 2 data clustered sampling data will be performed to evaluate correlational structure of the PCOI data. Information generated in Round 2 will be used to develop a geostatistical model. This model will be used to predict the distribution of contaminants within the Tittabawassee floodplain.

The Round 1 grid sampling locations are intended to cover a range of terrain features that are thought to influence contaminant distribution in floodplain soils. These features include disturbed (i.e., agricultural) and undisturbed (forested) land uses, different distances from the river, and areas where deposition of sediments during flooding events could have occurred, as well as areas believed to be less prone to deposition.

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[1] The null hypothesis H_o, sometimes called the test hypothesis because it is the hypothesis being tested, <u>is a statement that the experimenter doubts to be true</u>. It is usually the opposite of the alternative hypothesis H_1. If the experimental results are not consistent with the null hypothesis, the null hypothesis is rejected; otherwise it is not rejected (Iman, 1995).

The results from the Round 1 grid sampling will identify locations for cluster sampling during Round 2. Cluster sampling will be conducted at locations representing the various spatial relationships being tested (e.g., near river/far river, disturbed/undisturbed) as well as locations with elevated and low-to-moderate contaminant (i.e., dioxin and furan) concentrations in soil.

The results from the Round 2 study will be used to develop a geostatistical model that will be used during the remedial investigation to help determine the extent of contamination within the floodplain.

Study Boundaries

Three scoping study areas located along the Tittabawassee River floodplain were identified for study. The scoping study areas were chosen so that the influence of distance on concentration and distribution of contaminants could be evaluated. The Tittabawassee River changes in characteristics from upstream to downstream. In its upper reaches, the river tends to run in a straight line and the floodplain is relatively narrow. As the river nears its confluence with the Shiawassee and Saginaw Rivers it begins to exhibit a degree of sinuosity and the floodplain widens considerably. The scoping study areas locations reflect these changes in the river's characteristics. Additionally, the selected study areas contain features that, based on a preliminary evaluation of available data, appear to influence dioxin and furan distribution in soil, such as distance from the riverbank, floodplain geomorphologic features (e.g., presence or absence of natural levees), soil characteristics, land use, and disturbance following deposition. The influence of these various factors on dioxin and furan concentration and distribution within the floodplain will be evaluated using samples collected from of each scoping study area.

Decision Rules

Data from the gridded and clustered sampling design will be used to construct 2-D semivariograms. An analysis of variance (ANOVA) will be also be performed to evaluate the relationship of observed concentrations and other physical features.

Directional semivariograms will be used to describe correlation ranges in directions parallel and perpendicular to the river and floodplain. Possible outcomes from these analyses are:

- Results show spatial correlation in concentrations in both downstream and transverse (cross-stream) directions (existing data slightly indicates this possibility).
- Results show spatial correlation in transverse direction (existing data more strongly indicates this possibility).
- Results show no spatial correlations for concentrations in soil.

If the semivariograms indicate significant correlation structure, the identified ranges will help to define optimal sampling distances in the two directions. In addition, these ranges, as well as the dependence of contaminant concentrations on the different spatial factors (proximity to river, disturbed/undisturbed areas), will support preparation of a geostatistically-based model. The geostatistically-based model can be used to predict concentrations of contaminants in soil along the floodplain. Correlations between contaminant concentrations and other potentially related factors (e.g., TOC, grain size distribution parameters, flood recurrence) will also be explored, as possible additional constraints to the geostatistical model. If such secondary correlation relationships are identified, these data may provide the basis for development of a more robust co-kriging model that can be developed with more easily collected and less-costly data (such as TOC or grain size analyses).

In parallel with the geostatistical analysis of the data, an ANOVA analysis will be used to explore differences between different floodplain classifications (for example, disturbed/undisturbed; depositional/not depositional areas). ANOVA is a standard statistical technique to determine differences among populations or subgroups of interest. The method relies on differences in variance both across and within subpopulations of interest. "Nested ANOVA" is a technique that explores overlapping sources of variability in the data. In the floodplain soils scoping study sampling, sources of variability include the following:

- Laboratory measurements (as estimated by laboratory duplicate results)
- Sampling techniques, commonly referred to as "sampling error" (as estimated by field duplicate results)
- Small-scale variability in concentrations (as estimated by collocated samples)
- Larger-scale variability in concentrations (as estimated by the samples collected at different grid node locations) within a sampled area
- Larger-scale variability in concentrations among sampled areas (as estimated by samples collected from different portions of the scoping areas [e.g., disturbed versus undisturbed areas and areas close to the bank versus areas close to the 100-year floodplain])

The results of the ANOVA will provide information on statistical differences between contaminant concentrations in subgroups of interest in the floodplain (e.g., statistical difference between concentrations in disturbed versus undisturbed areas). This information related to contaminant distributions, along with other investigations of contaminant fate and transport processes, will be used to refine the CSM and plan sampling as part of the remedial investigation of the Tittabawassee River floodplain soils.

Acceptable Limits on Decision Errors

Scoping study sites have been selected to cover both disturbed and undisturbed areas to observe differences in concentrations relative to extent of land disturbance.

A gridded sampling approach has been proposed for the scoping study sites in Round 1 to limit decision errors by systematically observing changes in concentrations in soil with differences in physical site factors such as topography, TOC, and grain size. The subsequent clustered sampling approach in Round 2 will further evaluate the spatial correlations between concentrations and physical site factors.

Representativeness of the grid spacing will be evaluated through collection of collocated samples at 10 percent of the sample locations. The collocated samples will be placed to reflect the different physical features that may influence contaminant distribution:

- Locations near the Tittabawassee River where depositional features are present
- Locations further away from the Tittabawassee River where depositional features are not present
- Locations in disturbed areas
- Locations in undisturbed areas

Collocated samples that are representative of these four floodplain conditions will be randomly selected from the overall floodplain sampling grid in each scoping area. Collocated samples will be located at randomly selected orientations and randomly selected distances between grid nodes (random distances that are less than or equal to half the distance to the next closest grid node).

Control of decision errors associated with sampling and analysis will be achieved through adherence to procedures specified in the Quality Assurance Project Plan (QAPP).

Optimized Sampling Design

The Round 1 scoping area grid sampling design is based on a systematic random sampling approach. A random approach requires little or no prior knowledge of material distribution and relies on random chance probability theory, where each sampling location has an equal and known probability of being selected so that sampling error can be accurately estimated (MDEQ 2002). Systematic random sampling is an extension of simple random sampling, but is more efficient in that it introduces a systematic element (that is, regular spacing of locations, initiated from a random starting point) to the program, assuring uniform coverage of the entire area being characterized.

The initial sampling design for each scoping study area consists of a relatively coarse (400-foot spacing) sampling grid deployed across an area that includes relatively equal proportions of “disturbed” (i.e., cultivated) and “undisturbed” (i.e., forested) land located near and distant to the bank of the river. Each grid was laid out generally parallel the river and was extended into certain areas to allow collection of roughly equivalent numbers of samples for each potential factor grouping (i.e., near/far, disturbed/undisturbed). Approximately 40 surface soil (0 to 0.5 feet bgs) samples will be collected in each scoping study area.

The Round 2 scoping area cluster sampling design will be centered on locations that represent the various spatial relationships being tested (e.g., near river, disturbed) and nodes with elevated and low-to-moderate dioxin/furan concentration will be represented in this sampling program. The cluster sampling will be used to test various spatial relationships associated with the distribution and concentration of dioxin and furans found in floodplain soils A total of 20 cluster samples will be collected around each selected grid node. Typically, the cluster sample locations will be placed around the central sample at logarithmically increasing distances (1, 10, 30, 100, and 300 feet) and extending radially in four different directions (parallel, and perpendicular to the Tittabawassee River). However, the orientation, spacing, and extent of each cluster array will be adjusted to ensure that cluster sample locations fall within an area that represents the spatial relationship being tested.

DQO 2: Identification of Linkages between Sediment Contaminants and Occurrence and Distribution of Contaminants in Floodplain Soils

Problem Statement

Flooding events result in the deposition of sediments, and sediment-bound contaminants onto the floodplain. It is expected that relatively larger amounts of sediments will be deposited on the floodplain close to the banks of the river, while relatively lesser quantities will be deposited as one moves away from the riverbank. These depositional patterns may also influence contaminant distribution in floodplain soils. Episodic settling, resuspension, and burial of solids and particle-associated contaminants also may occur during flood stage.

Additional data are needed to assess conditions at the surface and at depth in floodplain soils and river sediments so as to better understand the relationships between floodplain soils and adjacent river sediment, and to better understand the vertical distribution of dioxins and furans in both media. Three specific questions will be addressed in the studies conducted as part of the scoping study:

- Are there similarities in floodplain and sediment lithologic characteristics, suggesting a relationship between floodplain soil and sediment contaminants?
- Are there similarities in concentrations of dioxins and furans in floodplain soils and sediments?
- Are there similarities in sediment deposition rates onto floodplain soils between the upper and lower reaches of the Tittabawassee River?

Decisions to be Made

Based on the three problems statements described above, there are three hypotheses will be evaluated regarding the linkages between contaminants in sediments and floodplain soils. The purpose for these hypotheses statements is to further evaluate the potential transport and deposition of sediment-bound contaminants onto floodplain soils. Data collection during this scoping study to evaluate these hypotheses are intended to refine the preliminary CSM and to provide information for use in developing the RI for the floodplain.

Hypothesis Statement 2A:

H_o: Floodplain soil and river sediment do not share similar lithologic and physical characteristics.

H_1: Floodplain soils and river sediments share similar lithologic and physical characteristics, suggesting a direct relationship between floodplain soils and adjacent river sediments..

Hypothesis Statement 2B:

H_o: Floodplain soils and river sediments do not have similar dioxin and furan distributions at depth.

H_1: Surface and subsurface floodplain soil and river sediment have similar dioxin and furan distributions, suggesting a direct relationship between floodplain soils and adjacent river sediments.

Hypothesis Statement 2C:

H_o: Rates of sediment deposition on the floodplain in the lower portion of the Tittabawassee River are not similar to those in the upper portion of the river.

H_1: Rates of sediment deposition on the floodplain in the lower portion of the Tittabawassee River are similar to those in the upper portion of the river, indicating a common pattern of sediment deposition throughout the floodplain.

Inputs to the Decisions

Hypothesis Statement 2A:

Lithologic Transect Study: Lithologic borings will be conducted in floodplain soils along transects that span each scoping study area, sediments in the river, and tie into soils on the opposite riverbank. Observations of the lithology will be used to develop an understanding of the geologic and geomorphic processes governing the formation and ongoing evolution of the river and floodplain system. These observations will provide a long-term (geologic time) context for interpretation of the shorter-term (decadal) observations of solids transport within the river and deposition onto the floodplain, to be evaluated from other studies conducted as part of this scoping study investigation. These other studies include observations of soil/sediment physical properties (grain size and TOC), measures of historical sedimentation rates onto floodplain soils using radiological tracers (geochronological analysis), dendrogeomorphic investigations, and measurements of vertical contaminant distributions.

Sediment and Floodplain TOC/Grain Size Analysis. Sediment and floodplain samples collected as part of the scoping grid and clustered sampling activities described previously will be analyzed for TOC and particle size distribution. These physical parameters will be used to develop an understanding of the physical structure of the sediment bed and floodplain soils, supporting a more general understanding of the transport processes that govern erosion/resuspension, transport, and deposition of sediments in the riverbed and floodplain.

Hypothesis Statement 2B:

Floodplain and sediment vertical characterization sampling (dioxin and furan analyses). Continuous soil and sediment cores extending from the ground surface to the water table (estimated to be at approximately 4 feet bgs) will be finely segmented and used for vertical characterization of dioxin and furan concentrations. These data, combined with geochronological analyses (conducted on the same core samples), will allow solids deposition histories to be coupled with historical contaminant loadings. This will provide further information about historical transport of contaminants in the sediment bed and floodplain soil column.

Hypothesis Statement 2C:

Floodplain and sediment vertical characterization sampling (geochronological analyses). Continuous soil and sediment cores extending from the surface to a depth that is approximately four feet below the apparent river bottom on the floodplain, and to the base of unconsolidated sediment within the river, will be finely segmented and used for geochronological analysis (i.e., radionuclide measurements). Observations of the vertical distributions of radiological tracers (Cs-137, Pb-210) will provide information on the long-term historical deposition rates of sediments and floodplain soils in depositional areas, and will also serve to indicate areas where little on no deposition is taking place. Pairing these data with observations of the vertical distribution of contaminants (described previously) will allow solids deposition histories to be coupled with historical contaminant loadings, making it possible to draw conclusions about historical transport of contaminants to the sediment bed and floodplain soil column.

Dendrogeomorphic measurement techniques. These are based on the general observation that primary lateral roots of selected species of tree are typically located at or near the ground surface at germination of the tree, and remain at approximately the same vertical elevation throughout the life of the tree. This characteristic makes it possible to excavate down to the primary laterals and compare the depth of deposited soils with the age of the tree (obtained by coring the tree and counting rings) to determine a net deposition rate over the tree's lifespan. Studying trees of different ages in the same location allows one to detect changes in deposition rates over time as well. Deposition rates measured with this method are less sensitive to the disturbances that can confound radionuclide-based measurements.

Study Boundaries

Hypothesis Statement 2A:

Subsurface lithologic borings will be advanced using direct-push techniques to a depth consistent with 4 feet below the river bed adjacent to each of the scoping study area (bottom of river/top of sediment will be determined from bathymetry data), or 2 feet into the underlying native glacial till, whichever is encountered first. The soil cores will be obtained at 200-foot intervals along each scoping study area transect. Sediment cores will be collected at three locations spanning the river. The sediment cores will be advanced using vibracoring (or similar technique) to the depth at which unconsolidated material is no longer present and native material (e.g., till) is encountered.

Hypothesis Statement 2B:

The vertical characterization soil cores will be obtained from the three scoping study areas (see DQO 1) using direct push equipment at transect locations that represent the geospatial (i.e., near the river, far from the river) and land use (i.e., disturbed or undistributed) conditions.

Hypothesis Statement 2C:

Data collection in support of the sediment deposition evaluation will be conducted in Scoping Study Area 3. The study will supplement geochronological and dendrogeomorphic data collected under a previous effort in Scoping Study Areas 1 and 2. The evaluation will consist of a dendrogeomorphic study at three locations along the undisturbed portion of the lithologic core transect and geochronological analysis of five cores taken near the trees selected for the dendrogeomorphic study.

Decision Rules

Formal decision rules have not been developed to evaluate these hypotheses. They will be evaluated using a weight of evidence approach, as described below:

Hypothesis 2A: Grain size and TOC analyses, and boring logs developed from the lithologic transects between sediments and floodplain soils will be compared to observe for similarities which may show the relative magnitude of sediment deposition onto floodplain soils.

Hypothesis 2B: The vertical trends in dioxin and furan concentrations between floodplain soils and sediments will be compared. Higher concentrations at depth in floodplain soils may indicate that sediments deposited onto the floodplain historically may have had higher dioxin and furan concentrations compared with more recent times. Dioxin and furan congener distributions in floodplain soils and sediments will be compared to observe for similarities. With the cessation of historic releases, it is possible that current suspended solid flows are no longer adding contaminants to instream sediments or floodplain soils downstream of the facility. Vertical profile results may be useful in evaluating this possible trend.

Hypothesis 2C: The results from geochronological and dendromorphological analyses will be combined with the dioxin and furan vertical profiling data to better understand differences in sedimentation rates at different locations in Tittabawassee River floodplain soils. These data will be combined with observations of contaminant concentrations, congener distributions, soil/sediment physical properties and adjacent floodplain data and lithologic observations will be used to draw conclusions about exchange of solids and contaminants between the river and floodplain.

Acceptable Limits on Decision Errors

Limits on decision errors will be controlled through adherence to standard operating procedures in sample collection, and through adherence to the QAPP for laboratory analyses.

The deposition rates measured with dendromorphological analysis are less sensitive to the disturbances that can confound radionuclide-based measurements, and will be used as a check on geochronological measurements.

Optimized Sampling Design

A transect that goes through and adjacent to each of the three scoping study areas will be established. Samples will be collected along each transect and the data generated from these samples sets will be used to test Hypotheses 2A through 2C. The sampling design for the floodplain soil and river sediment transect sampling program is as follows:

- **Lithologic Core Transect Sampling.** To test the first set of hypotheses, subsurface lithologic borings will be placed along transects that span each scoping study area. Soil cores will be advanced using direct push techniques to a depth consistent with 4 feet below the riverbed adjacent to the scoping study area (bottom of river/top of sediment will be determined from bathymetry data), or 2 feet into the underlying native glacial till, whichever is encountered first. The soil cores will be obtained at 200-foot intervals along each scoping study area transect . Sediment cores will be collected at three locations spanning the river. The sediment cores will be advanced using vibracoring (or similar technique) to the depth at which unconsolidated material is no longer present and consolidated native material is encountered.
- **Vertical Characterization Sampling.** The second set of hypotheses will be tested by selecting a subset of the soil cores and all sediment cores from the lithologic core transect sampling program and segmenting them into 0.5-ft (upper 3 feet) and 1-ft (remainder of core) intervals. Initially, each 6-inch interval from a core will be analyzed to determine the concentrations of dioxins and furans (17 congeners) and TOC. Grain size analysis will also be performed. The need for analysis of the deeper samples will be determined by the results for the preceding sample interval (e.g., if dioxins and furans are detected in the 3.0 to 4.0-ft interval, then the 4.0 to 5.0 sample will be analyzed). The vertical characterization soil cores will be obtained using direct push equipment at transect locations that represent the geospatial (i.e., near the river, far from the river) and land use (i.e., disturbed or undistributed) elements discussed into the geospatially-based design for floodplain characterization described for Hypothesis 1.
- **Sediment Deposition Evaluation.** Data will be collected from Scoping Study Area 3 to evaluate the rate of deposition on the floodplain. This information will be used to test the third set of hypotheses. These data will supplement dendrogeomorphic and geochronological data collected under a previous effort in Scoping Study Areas 1 and 2.

DQO 3: Exploratory Analysis of the Confluence Area

Problem Statement

Conditions in the confluence area between the Tittabawassee and Shiawassee Rivers are less well understood compared with upstream reaches along the Tittabawassee River. Existing data are limited and suggest that: sedimentation rates in the confluence area may be greater than those observed in the upper reaches of the Tittabawassee River and that trends in dioxin and furan concentrations in the area may be influenced by additional factors, such as the distance from the Tittabawassee River and/or frequency of flood recurrence. Therefore, the purpose for these studies is to obtain exploratory data that will be used to better understand sedimentation rates and the dioxins and furan trends in distribution in surface soil in the lower portions of the Tittabawassee River study area. These data would be used to develop an appropriately located and scaled scoping study, such as that described previously for Scoping Study Areas 1, 2 and 3.

Decisions to be Made

The following pairs of null and alternate hypotheses will be tested using data collected during the confluence area exploratory assessment:

1. –H_{0A}: Rates of sediment deposition on the floodplain in the lower portion of the Tittabawassee River are not similar to those in the upper portion of the river.

   - H_{1A}: Rates of sediment deposition on the floodplain in the lower portion of the Tittabawassee River are similar to those in the upper portion of the river, indicating a common pattern of sediment deposition throughout the floodplain.
2. –H_{0B}: Trends in dioxin and furan concentrations across the confluence area are not related to distance from the Tittabawassee River.

   – H_{1B}: Trends in dioxin and furan concentrations across the confluence area are related to distances from the Tittabawassee River and this information can be used to help develop the remedial investigation of the Tittabawassee River.
3. –H_{0C}: Trends in dioxin and furan concentrations across the confluence area are not related to frequency of flood recurrence.

   – H_{1C}: Trends in dioxin and furan concentrations across the confluence area are related to frequency of flood recurrence, and this information can be used to help develop the remedial investigation of the Tittabawassee River.

Because this study is exploratory, its DQOs are presented at a fairly high level. Null hypothesis statements regarding the confluence area will be developed for subsequent studies that will be conducted after collection of these exploratory data.

Inputs to the Decisions

The exploratory assessment will consist of a sediment deposition evaluation and a surface soil sampling program along two mutually perpendicular transects through the confluence area between the Tittabawassee and Shiawasee Rivers. The surface soil samples will be analyzed for dioxins and furans (17 congeners), TOC, and grain size.

Study Boundaries

The exploratory assessment will consist of a surface soil sampling program and a sediment deposition evaluation along two mutually perpendicular transects through the confluence area between the Tittabawassee and Shiawassee Rivers. Transect A will extend from Scoping Study Area 3 through the confluence area to the southern bank of the Shiawassee River and Transect B will consists of west-east trending line crossing several different flood event (i.e., 1-, 10-, 50-year) boundaries within the confluence area between the Tittabawassee and Shiawassee Rivers. The dendrogeochronological study will be conducted at three locations along each transect, and geochronological analysis will be conducted on five 4-foot-deep cores taken in the vicinity of the dendrogeochronological study locations.

Decision Rules

Because this is an exploratory investigation, formal decision rules have not been developed for evaluation of these data.

Acceptable Limits on Decision Errors

Limits on decision errors will be controlled through adherence to standard operating procedures in sample collection, and through adherence to the QAPP for laboratory analyses.

Optimized Sampling Design

The surface soil sampling program will be conducted along two mutually perpendicular transects through the confluence area between the Tittabawassee and Shiawassee Rivers:

- Exploratory Transect A consists of a north-south trending line extending from Scoping Study Area 3 through the confluence area to the southern bank of the Shiawassee River. Data from surface soil (0 to 0.5 feet bgs) along Transect A will be used to identify trends in dioxin and furan distribution that may be related to distance from the Tittabawassee River and/or proximity to the Shiawassee River. The soil sampling design for Transect A consists of collecting surface soil samples at a spacing of 400 feet near the Tittabawassee River (replicating the grid spacing in Scoping Study Area 3) and at a spacing of 800 feet further away from the Tittabawassee River.

- Exploratory Transect B consists of west-east trending line crossing a portion of the floodplain where the individual floodplains are distinct (e.g., the edge of 10-year floodplain is clearly distinguishable from that of the 100-year floodplain). Data from surface soil (0 to 0.5 feet bgs) along Transect B will be used to identify trends in dioxin and furan distribution that may be related to the frequency of flooding. Regularly-spaced sample locations along this transect were chosen to represent the gradient from the 1-year floodplain to the 100-year floodplain.

The surface soil samples from the exploratory transects will be analyzed for dioxins and furans (17 congeners), TOC, and grain size.

The sediment deposition evaluation for the confluence area will be similar to that described for Scoping Study Area 3, in that a dendrogeochronological study will be conducted at three locations along both Transects A and B, and geochronological analysis will be conducted on five 4-foot-deep cores taken in the vicinity of the dendrogeochronological study locations along Transects A and B.

DQO 4 Understanding Dioxin and Furan Gain and Loss in the Lower Tittabawassee River During a Typical Wet Weather Event

Problem Statement

Previous studies of the Tittabawassee River have suggested that hydrophobic contaminants are primarily transported with suspended solids. However, the extent to which this transportation mechanism plays in the transport of organic contaminants such as dioxins and furans is not known. With the cessation of historic releases, it is possible that current suspended solid flows are no longer adding dioxins and furans to instream sediments or floodplain soils downstream of the facility. It is likely that sediment and floodplain soil along the river contain dioxins and furans and may act as secondary sources for redistribution of the contaminants within the system. However, little is known with regard to the extent that processes such as floodplain runoff, bank erosion, or exchange with the Tittabawassee River sediment bed contribute to gain in contaminant load with respect to downstream transport in the river.

There is no formal hypothesis statement associated determining the concentration of dioxin and furans in suspended sediments. No data are currently available to address this aspect of the CSM. Data collected as part of this will be used as a first step towards quantifying contaminant load gain through the river and floodplain and refining the CSM.

Inputs to the Decisions

High-volume water column samples will be collected during high flow events (i.e., flows consistent with a 1 year FEMA flood event of approximately 10,000 cfs or greater) to allow analysis of dioxin and furan concentrations in suspended sediment. Collection of samples will be targeted for the rising limb of the wet-weather event, the peak of the event and post-event during the decline of the river hydrograph. The data collected under this effort will be used to quantify the particulate concentration of dioxins and furans at the upstream and downstream boundaries of the study area.

Study Boundaries

High-volume water column samples will be collected during high-flow events to allow analysis of dioxin and furan concentrations in suspended sediment. Samples will be collected at the Currie Parkway Bridge upstream of the city of Midland, and at the Center Road Bridge just upstream of the confluence of the Tittabawassee River with the Saginaw River.

Decision Rules

As described previously, the purpose for this sampling is to quantify the particulate concentration of dioxins and furans in suspended sediments at the upstream and downstream boundaries of the study area. The concentrations in suspended sediments will be compared between upstream and downstream locations to determine if concentration trends increase with distance downstream, or with specific events, such as flooding.

Acceptable Limits on Decision Errors

Limits on decision errors will be controlled through adherence to standard operating procedures in sample collection, and through adherence to the QAPP for laboratory analyses.

Optimized Sampling Design

The high-volume water column sampling program will be conducted using samples collected at the Currie Parkway Bridge upstream of the city of Midland, and at the Center Road Bridge just upstream of the confluence of the Tittabawassee River with the Saginaw River. The high-volume water column samples will be collected during high-flow events (i.e., flows consistent with a 1-year FEMA flood event of approximately 10,000 cfs or greater) to allow analysis of dioxin and furan concentrations in in-river suspended sediment. Samples will be collected using a depth- integrating isokinetic water sampler (US DH-76). Collected samples will be composited in a 20-liter glass carboy and submitted to a dioxin laboratory for filtration and analysis of dioxins and furan congeners (17 congeners) and for total suspended solids (TSS). Collection of samples will be targeted for the rising limb of the wet weather event, the peak of the event and post-event during the decline of the river hydrograph.

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